J|A|C|S
COMMUNICATIONS

Published on Web 09/01/2006

Rapid Production of Metal−Organic Frameworks via Microwave-Assisted Solvothermal Synthesis

Zheng Ni and Richard I. Masel*

Department of Chemical and Biomolecular Engineering, Materials Chemistry Program, 600 S Mathews, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received May 28, 2006; Revised Manuscript Received August 22, 2006; E-mail: r-masel@uiuc.edu

The objective of this paper is to describe a very rapid method for the synthesis of metal-organic frameworks (MOF) that allows the synthesis to be completed in minutes, and new materials to be made. MOFs have been a focus of intense activity in recent years because of their extremely high porosities and tailorable molecule cavities. Such materials have been studied for a variety of applications, such as hydrogen storage, selective adsorption, nonlinear optical materials, and as catalysts.[1−8] So far all of the reported syntheses were 1/2 day to multiday procedures. Yaghi and co-workers produced a large number of MOFs via solvothermal synthesis. The process took 1−7 days.[2] Lin and co-workers created a nonlinear optically active MOF material through a multiday hydrothermal synthesis.[3] Willams and co-workers reported a thermal stable structure through a 12 h solvothermal synthesis.[4] Kim and co-workers reported several catalytically active homochiral metal−organic materials through a two-day liquid diffusion method[5] or solvothermal method.[6] Suslick and co-workers reported polar PIZA-1 structure by a two-day solvothermal synthesis,[7] and a nonpolar PIZA-4 structure through one-week deprotonating vapor diffusion.[8]

Microwave-assisted processes have been used to produce small metal and oxide particles. Such processes can involve heating a solution with microwaves for a period of an hour or more to produce nanosized crystals of metal. Typically, particle sizes are 15 nm. The expectation with microwave heating is that small particles, on the order of 10−15 nm, will form.[9] Microwave synthesis to give 5−20 nanometer sized particles of oxides is also known.[10] Here we present a new synthetic approach that we named "microwave-assisted solvothermal synthesis", which allows high quality metal−organic framework crystals to be synthesized in under a minute. The properties of the crystals made by the microwave-assisted process are of the same quality as those produced by the standard solvothermal process, but the synthesis is much more rapid. Although the microwave method usually cannot yield crystals with a size big enough for single X-ray analysis, its homogeneous effects could create a uniform seeding condition; therefore the size and shape of the crystals can be well controlled and the synthesis cycle can be largely shortened for many practical applications.

We report on the assembly of three known MOFs, namely IRMOF1, IRMOF2, and IRMOF3, through a rapid microwave-assisted methodology. The microcrystals have relative uniform size and identical cubic morphology. We also demonstrate that crystal size can be varied from micrometer down to submicrometer scale by manipulating the concentration of the reactant solution.

For the synthesis of microcrystals of IRMOF-1, 2, and 3, a mixture of metal precursor and corresponding spacing ligand was dissolved in *N*,*N*-diethylformamide (DEF) solvent.[11] To create a homogeneous seeding environment, the mixture is thoroughly stirred for 15 min to get a clear solution. In a typical synthesis, an exact amount of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 g, 0.67 mmol) and 1,4-benzene-dicarboxylate acid ($BDCH_2$) (0.083 g, 0.50 mmol) are dissolved in 10 mL of the *N*,*N*′-diethylformamide (DEF) resulting in a clear solution. An amount of 1 mL of the solution was sealed in a 4-ml Pyrex sample vial. The vial was then placed inside a hood behind a blast shield and heated by a microwave synthesizer (model 520A from Resonance Instrument Inc.) at 150 W for 25 s. A yellow suspension formed after the microwave treatment. The product was rinsed (centrifuged and redispersed in DEF by sonicating) three times before analysis.

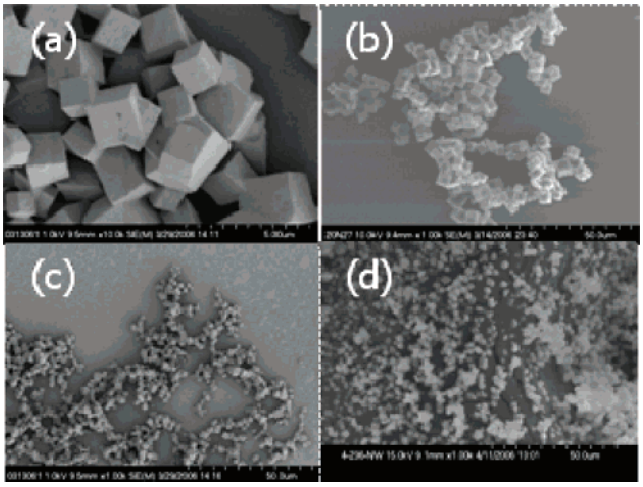

Figure 1. (a) Enlarged SEM image of micro IRMOF-1; (b) SEM image of micro IRMOF-1; (c) SEM image of micro IRMOF-2; (d) SEM image of micro IRMOF-3.

The resulting suspended particles of IRMOF-1 were found to be microsized cubic crystals, as shown in Figure 1a,b, with an average size of 4 ± 1 μm. Particles of IRMOF-2 and -3 also show the same cubic morphology with a different size. The cubic structures of all these MOF species are further supported by X-ray powder diffraction (XRPD) results as shown in Figure 2. Notice that the crystals have a structure that closely matches that reported previously.

Smaller particles can be obtained by reducing the reactant concentration in a starting solution. In the synthesis of small IRMOF-1 crystals, the concentration of $BDCH_2$ was diluted from 0.05 to 0.0002 M, and the amount of zinc precursor was changed correspondingly so the metal/ligand molar ratio remained 4:3. The microwave treatments were also extended up to 90 s when the solution was diluted. An ∼8 s increase in heating time is needed when the concentration is diluted in half. Figure 3 shows that particle size varied as the reactant concentration changed. Submicrometer-sized crystals were formed when the reactant concentration was scaled down to a few mM. The edge and vertex of the submicrometer-sized crystal are observed to be less sharp than those of microsized crystals, as shown in Figure 4. The effect of

10.1021/ja0635231 CCC: $33.50

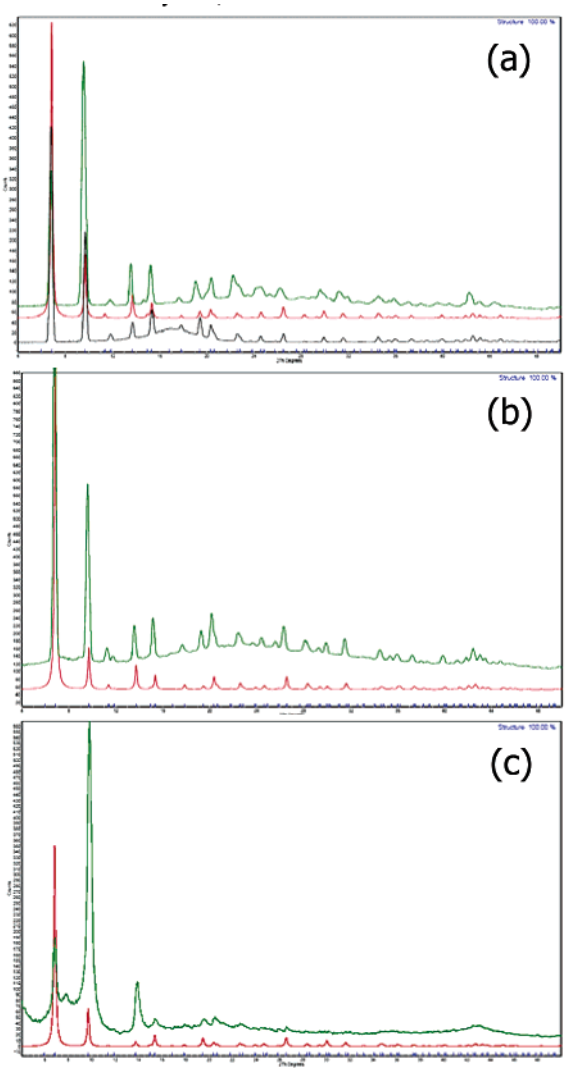

Figure 2. XRPD patterns of (a) IRMOF-1, (b) IRMOF-2, and (c) IRMOF-3 prepared by the solvothermal synthesis of Eddaoudi, M. et al. (black) and by microwave-assisted solvothermal synthesis (green) and a simulated XRPD curve based on the published structure of Eddaoudi, M. (red).

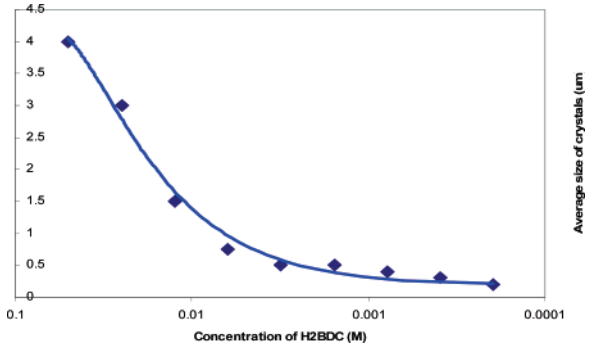

Figure 3. Estimated average size of IRMOF-1 microcrystal versus concentration of BDCH2 in the reactant solution.

microwave reaction time on crystal formation is also investigated. No crystal formation is observed when the microwave time is under 20 s. By varying the reaction time from 25 s to 1 min, the size of the microcrystals does not change remarkably.

We can speculate how the microwave is able to enhance the crystal growth process. In the conventional solvo-thermal growth process, crystals nucleate near the walls or on dust particles. That results in slow growth because there are very few seeds. In the microwave-assisted process, though, we observe crystals throughout the bulk of the solution probably because local superheating of the DEF solvent leads to hot spots that nucleate crystal growth. More seeds lead to faster growth and higher yields. Once the seeds start to grow, available reactants are quickly depleted. Therefore the size of the crystals can be varied by adjusting the reactant concentration. The ability of the microwave technique to control the nucleation process leads to a narrow size distribution, because all of the crystals are nucleated at once. It also allows new types of MOFs to be discovered readily since the growth process is not depending on nucleation on the walls or dust particles.

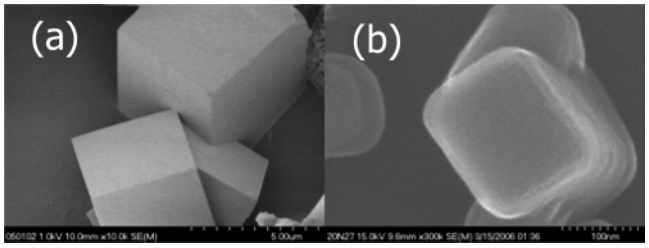

Figure 4. Enlarged SEM images of IRMOF-1 synthesized from concentration of BDCH2 at (a) 0.05 M and (b) 0.0002 M.

One caution with the method: heating a closed bottle containing volatile solvents and nitrates can produce an explosion. Microwaves create hot spots that can accelerate the explosion. In particular the pressure in a vessel containing a volatile solvent (e.g., ethanol) can be much higher than with conventional synthesis. Microwave leakage is also dangerous. We perform the experiment in a hood and place a blast shield in front of the sample vial. Readers are advised to take appropriate precautions.

Acknowledgment. We gratefully acknowledge financial support from the Defense Advanced Research Projects Agency (DARPA) under U.S. Air Force Grant FA8650-04-1-7121. The authors have applied for a patent for this method.

References

(1) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.

(2) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Yaghi, O. M.; Eddaoudi, M.; Li, H.; Kim, J.; Rosi, N. U.S. patent 20030004364A1.

(3) Lin, W.; Wang, Z.; Ma, L. *J. Am. Chem. Soc.* **1999**, *121*, 11249.

(4) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, L. D. *Science* **1999**, *283*, 1148.

(5) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon Y. J.; Kim K. *Nature*, **2000**, *404*, 982.

(6) Dybtsev, D. N., Nuzhdin, A. L.; Chun, H.; Bryliakov, P. K.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.*, **2006**, *45*, 916.

(7) Kosal, M. E.; Chou, J.-H.; Wilson, S. R.; Suslick, K. S. *Nat. Mater.* **2002**, *1*, 118.

(8) Smithenry, D. W.; Wilson, S. R.; Suslick, K. S. *Inorg. Chem.* **2003**, *42*, 7719.

(9) (a) Panda, A. B.; Glaspell, G.; El-Shall, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 2790. (b) Lu, Q.; Gao, F.; Li, D.; Komarneni, S. *J. Mater.* 2005, *1*, 1.

(10) Tompsett, G. A.; Conner, W. C.; Yngvesson, K. S. *ChemPhysChem.* **2006**, *7*, 296.

(11) (a) IRMOF2 synthesis: The exact amount of 2-bromoterephthalic acid (2-BrBDCH$_2$) (0.040 g, 0.160 mmol) and zinc nitrate tetrahydrate Zn(NO$_3$)$_2$·6H$_2$O (0.0594 g, 0.20 mmol) were dissolved in 15 mL of diethylformamide. The solution was then sealed with a Pyrex sample vial and heated at 150 W for a reaction time of 40 s. A yellow suspension formed after the microwave treatment. (b) IRMOF3 synthesis: The exact amount of 2-aminoterephthalic acid (2-amino-BDCH$_2$) (0.2 g, 0.67 mmol) and zinc nitrate tetrahydrate Zn(NO$_3$)$_2$·6H$_2$O (0.0913 g, 0.504 mmol) were dissolved in a mixture of 39 mL of diethylformamide and 3 mL of ethanol. The solution was then sealed with a Pyrex sample vial and heated at 150 W for a reaction time of 35 s. An orange suspension formed after the microwave treatment.

JA0635231